

**EVIDENCE FOR A LATE-STAGE THERMAL OVERPRINT IN ALH 84001 AND IMPLICATIONS FOR BIOMARKERS.** C.K. Shearer<sup>1</sup> and A. Brearley<sup>2</sup>, <sup>1</sup>Institute of Meteoritics, <sup>1,2</sup>Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, USA.

**Introduction:** Deciphering the thermal history of ALH 84001 is essential in evaluating the evidence for possible fossil life in that martian meteorite. The focus of this debate has primarily involved the temperature of carbonate formation and has virtually ignored the post-depositional history of the carbonates [1–7]. Here, we provide evidence for a transient, high-temperature thermal pulse following carbonate deposition and describe possible effects on the carbonates that have previously been attributed to low-temperature processes and biogenic activity.

**Evidence for a Post-Carbonate High-Temperature Event:** There are at least three lines of evidence that suggest that these low-temperature carbonates [1–3] were exposed to a rapid, high-temperature event: disruption of the carbonate globules during the formation and mobilization of the shock glass, the formation of olivine inclusions in the orthopyroxene and the amorphous character of sheet silicates near the carbonate-glass boundary.

The degree of disruption of the carbonate globules by the mobilization of shock glass is well illustrated in Figures 1–3. Figure 1 shows relatively undisturbed, zoned carbonate. The zoning is particularly complex as the carbonates precipitated within small cracks in the orthopyroxene, dissolution voids and adjacent to crushed fragments of orthopyroxene. Figure 2 shows a similarly zoned carbonate globule with its base crushed and injected with shock glass. Within the crushed zone, carbonate cleavage fragments provide evidence that this texture does not represent carbonate growth within shock glass voids. Also the complex zoning observed in the individual fragments were not a product of carbonate melt interaction or growth in glass voids, but simply reflects complex carbonate growth as illustrated in Figure 1. Figure 3 also illustrates the disruption and transport of carbonate globules by the shock melt. Clearly, in Figure 3, the carbonate has been pulled from the orthopyroxene wall on which it had initially crystallized. The crushed zone between the carbonate and the orthopyroxene consists of carbonate cleavage and orthopyroxene fragments immersed in shock glass. Displacement is on the order of 10–30  $\mu\text{m}$ . Even greater displacement of carbonate globules (200–300  $\mu\text{m}$ ) has been observed. Evidence for a late-stage shock event has been recognized by Treiman [8].

A second line of evidence for the carbonate experiencing a high-temperature event is the olivine “inclusions” in the orthopyroxene adjacent to the carbonate.

The olivine occurs only near fractures that contain disrupted carbonate. Note the absence of olivine in Figure 1 and the abundance of olivine in Figure 2. The inclusions are irregular in shape and range in size from approximately 40  $\mu\text{m}$  to submicron. The inclusions are in sharp contact with the enclosing orthopyroxene, and often contained small inclusions of chromite. The  $\delta^{18}\text{O}$  values of the olivine and orthopyroxene that were analyzed range from +4.3 to +5.3 ‰ and are indistinguishable from each other within analytical uncertainty. The  $\delta^{18}\text{O}$  values of the olivine is strong evidence that the olivine was not in isotopic equilibrium with the carbonate. In addition, the specific location of the olivine adjacent to fractures containing disrupted carbonates is highly suggestive of a non-magmatic origin. The olivine may have been formed by reduction of magmatic orthopyroxene and spinel during this late, high-temperature event.

A third line of evidence for post-depositional heating of the carbonates has been described by Brearley [9]. Minute sheet silicates within the carbonate are not observed in the shock glass and appear to be amorphous near the carbonate-glass interface. This implies that the glass and the carbonate interface were involved in a late-heating event.

**Conditions of High-Temperature Event.** Mineral geothermometers using olivine and associated phases (orthopyroxene, spinel) record a high-temperature, subsolidus environment. Fe-Mg exchange between olivine and chromite inclusions in the olivine gives equilibrium temperatures of between 850° to 900°C. The olivine-orthopyroxene geothermometer yields temperatures of between 800° to 900°C.

The textures implying mobilization of the carbonates indicate flow of the shock melt. The viscosity of the shock-glass at various temperatures can be calculated from its chemical composition [10]. Melts with viscosities of  $10^8$  poise ( $\log_{10}$  viscosity = 8) have the consistency of cool asphalt or very thick paste. In order to reproduce the textural relationships between the carbonate and shock-glass, the viscosity of the shock-glass must have been less than  $10^6$  poise indicating that it was injected at temperatures exceeding 1000°C. This agrees with previous qualitative estimates for the flow of plagioclase glass [11,12].

In such scenario, would a high temperature thermal event destroy the delicate, low temperature chemical zoning observed in the carbonate? The de-

struction of the chemical zoning by chemical diffusion processes is not necessarily a final outcome to this thermal event. The chemical effects the thermal event has on the carbonates is dictated by the length of the event and the thermal diffusion profile across the carbonates. In a simple thermal model assuming a single 200  $\mu\text{m}$  vein of shock melt at a temperature of 1100°C intruded into an infinite carbonate layer at a temperature of 0°C, the carbonate adjacent to the shock-glass will be heated to 400°–500°C and will fall to less than 50°C within seconds of the event. Under more complex scenarios, it is conceivable that the carbonate was exposed to slightly higher temperatures (500°–600°C). The thermal event, however, is very short lived. If the diffusion coefficients of Mg and Fe in carbonate are similar to other rock-forming minerals at these temperatures ( $10^{-18}$  to  $10^{-21}$   $\text{cm}^2 \text{ sec}^{-1}$ ), this thermal event would have heated the carbonates to temperatures of 400°–600°C without destroying the intricate, low-temperature chemical zoning.

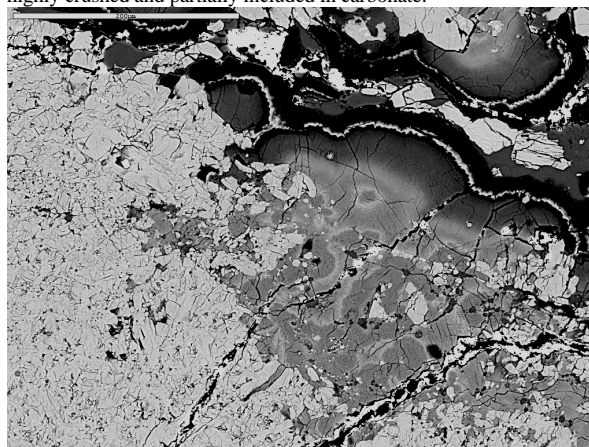
**Implications for biomarkers in ALH 84001.** This late stage heating event has a number of important implications for the origin of “biomarkers” in ALH 84001. First, this model explains the occurrence of magnetite in carbonate [13]. The concentration of magnetite in Fe-rich carbonate bands is produced because this carbonate composition is the least thermally stable and will produce the most magnetite on decomposition. At temperatures as low as 385°C, siderite decomposition can be detected [14,15], whereas magnesite and calcite are stable to temperatures of at least 650°C and 985°C, respectively [16]. The voids in the carbonates that are commonly associated with magnetite are produced by the loss of  $\text{CO}_2$  resulting from the decomposition of the siderite component in solid solution.

Second, the wide variability in  $\delta^{18}\text{O}$  observed in the carbonates may be attributed to this late thermal pulse. The Mg-rich carbonates have  $\delta^{18}\text{O}$  values between 18 and 22 ‰, whereas the  $\delta^{18}\text{O}$  of the Fe-rich carbonates is much more variable and lower (6–18 ‰) [3,17]. The effect of decarbonation is to decrease the  $\delta^{18}\text{O}$  value of the carbonate [18]. This could explain the lower and variable  $\delta^{18}\text{O}$  for the Fe-carbonates assuming the oxygen isotopic composition of the carbonates was similar prior to heating.

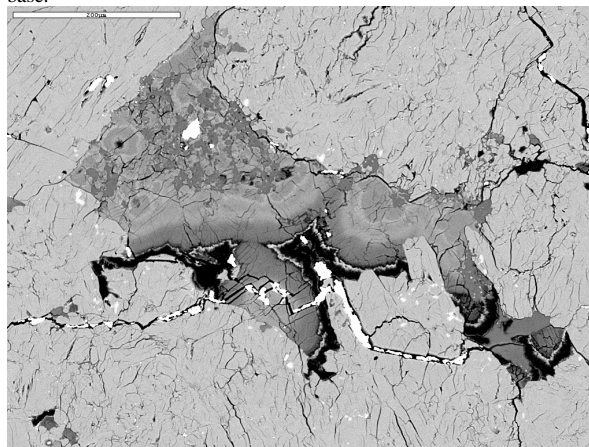
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**Fig. 1.** Complex zoning in carbonate globule. Orthopyroxene wall is highly crushed and partially included in carbonate.



**Figure 2.** Carbonates with complex zoning as shown above. The base of these carbonates are highly fractured and injected with shock-glass. Carbonate fragments are broken along cleavage planes. Olivine (irregular, small white masses) occurs in the opx adjacent to the carbonate base.



**Figure 3.** Carbonate globule displaced from opx wall. Carbonate cleavage fragments and crushed opx are entrapped in shock glass.

